Revealing Structural Polytypism In Layered Boron Nitride

Jakub Iwański[1], Krzysztof P. Korona[1], Mateusz Tokarczyk[1], Aleksandra K. Dąbrowska[1], Piotr Tatarczak[1], Izabela Rogala[1], Marta Bilska[1,2], Sławomir Kret[2], Anna Reszka[2], Bogdan J. Kowalski[2], Song Li[3], Adam Gali[3,4,5], Guillaume Cassabois[6], Bernard Gil[6], Johannes Binder[1], Andrzej Wysmołek[1]

[1] *Faculty of Physics, University of Warsaw, Pasteura 5, 02-093 Warsaw, Poland*
[2] *Institute of Physics, Polish Academy of Sciences, Lotników 32/46, 02-668 Warsaw, Poland*
[3] *HUN-REN Wigner Research Centre for Physics, P.O. Box 49, H-1525 Budapest, Hungary*
[4] *Department of Atomic Physics, Institute of Physics, Budapest University of Technology and Economics, Műegyetem rakpart 3., H-1111 Budapest, Hungary*
[5] *MTA-WFK Semiconductor Nanostructures Research Group, P.O. Box 49, H-1525 Budapest, Hungary*
[6] *Laboratoire Charles Coulomb (L2C), UMR 5221-CNRS-Université de Montpellier, F-34095 Montpellier, France*

Hexagonal boron nitride (hBN) as atomically flat two-dimensional insulator is an important component of many van der Waals heterostructures. It may serve as a substrate for the growth of other materials, as dielectric spacer or encapsulating layer protecting other materials from degradation, while enhancing their performance. However, layered boron nitride exhibits many interesting properties on its own. It can crystalize in several polytypes. The most popular polytype is hexagonal boron nitride with AA' stacking in which subsequent atomic layers are twisted by 60° with respect to each other. Other observed layered BN stackings are Bernal (bBN) and rhombohedral (rBN). Due to the shift of the subsequent layers, those polytypes exhibit different symmetry showing characteristic additional properties such as second harmonic generation, piezo- and pyroelectric effects [1]. The appropriate stacking sequence is of key importance for different applications. However, the identification of the polytype, as well as the ability to grow desired BN polytypes is still a big challenge.

In this work we show that impurity related UV photoluminescence in layered BN may serve as a polytype indicator. Zero-phonon lines at 4.10 eV and 4.14 eV with their phonon replicas presented in Fig. 1a) can be ascribed to a carbon dimer defect emission in hBN and rBN, respectively. This defect is very sensitive to different stacking sequences making polytype identification possible [2]. Our findings are supported by theoretical calculations, X-Ray Diffraction measurements, Transmission Electron Microscopy and Cathodoluminescence results. By using Metal Organic Vapor Phase Epitaxy (MOVPE) [3], the content of a particular polytype in BN layer can be influenced by combining different growth parameters, which opens up large possibilities for future applications.

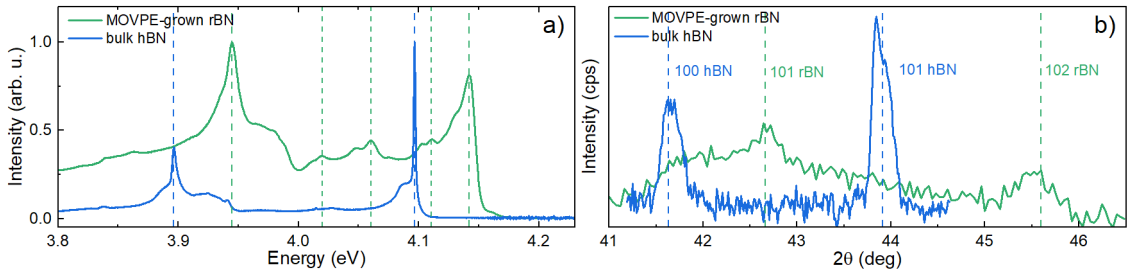

Fig. 1: a) PL spectra and b) XRD curves for MOVPE-grown rBN and commercial hBN. Dashed lines represent: a) ZPL and phonon replicas characteristic for a given polytype, b) peaks related to reflection from corresponding atomic planes.

[1] A. Rousseau, et al. *Phys. Rev. Mater.* **6.9**, 094009 (2022).
[2] K. P. Korona, et al. *Nanoscale* **15.22**, 9864-9877 (2023).
[3] M.Tokarczyk, et al. *2D Mater.* **10.2**, 025010 (2023).